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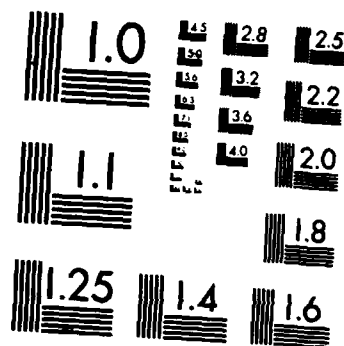
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CHEMICAL APPLICATION OF TOPOLOGY AND GROUP THEORY. 23.
A COMPARISON OF GRAPH-THEORETICAL AND EXTENDED HÜCKEL
METHODS FOR STUDY OF BONDING IN OCTAHEDRAL AND ICOSAHEDRAL BORANES

by

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of the $B_6H_6^{2-}$ octahedron the single positive eigenvalue of the K_6 graph corresponds to the results from the extended Hückel calculations. In addition, the parameters from the latter calculations indicate a ratio of 0.625 for the overlap of the unique internal orbitals of the trans atom pairs relative to cis atom pairs as compared with unity implied by an unweighted K_6 graph. In the case of the $B_{12}H_{12}^{2-}$ icosahedron the graph theory derived model is far less satisfactory since the single positive eigenvalue of the K_{12} graph disagrees with the four bonding core molecular orbitals (an A_{1g} and three triply degenerate T_{1u} molecular orbitals) found by the extended Hückel calculations after removing the effect of the mixing of core and surface bonding orbitals corresponding to the same irreducible representations. However, this core-surface orbital mixing raises the energy of the triply degenerate T_{1u} core molecular orbitals to antibonding levels so that the graph theory derived model fortuitously gives correct skeletal electron counts for the regular icosahedron despite this fundamental error.

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Abstract

The graph theory derived model for the bonding topology in the globally delocalized polyhedral boranes $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ is evaluated by comparison of the energies of the core molecular orbitals with those obtained by the 1962 LCAO-MO extended Hückel calculations of Hoffmann and Lipscomb. Of particular interest is how well the complete graphs K_6 and K_{12} used in the graph theory derived model approximate the bonding topologies of the unique internal orbitals (radial orbitals) of the octahedron and icosahedron, respectively. In the case of the $B_6H_6^{2-}$ octahedron the single positive eigenvalue of the K_6 graph corresponds to the results from the extended Hückel calculations. In addition, the parameters from the latter calculations indicate a ratio of 0.625 for the overlap of the unique internal orbitals of the trans atom pairs relative to cis atom pairs as compared with unity implied by an unweighted K_6 graph. In the case of the $B_{12}H_{12}^{2-}$ icosahedron the graph theory derived model is far less satisfactory since the single positive eigenvalue of the K_{12} graph disagrees with the four bonding core molecular orbitals (an A_{1g} and three triply degenerate T_{1u} molecular orbitals) found by the extended Hückel calculations after removing the effect of the mixing of core and surface bonding orbitals corresponding to the same irreducible representations. However, this core-surface orbital mixing raises the energy of the triply degenerate T_{1u} core molecular orbitals to antibonding levels so that the graph theory derived model fortuitiously gives correct skeletal electron counts for the regular icosahedron despite this fundamental error.

1. INTRODUCTION

Several years ago we developed a graph-theoretical approach for the study of the bonding topology in polyhedral boranes, carboranes, and metal clusters.^{2,3} Subsequent work has shown this approach to be very effective in relating electron count to cluster shape for diverse metal clusters using a minimum of computation. Metal clusters treated effectively by this approach include post-transition element clusters,⁴ osmium carbonyl clusters,⁵ gold clusters,^{6,7} platinum carbonyl clusters,^{6,8} and rhodium carbonyl clusters having fused polyhedra.^{9,10}

This graph-theory derived method uses ideas originating from Hückel theory.^{11,12} However, in order to eliminate the need for computation for determination of the signs of the energy levels, additional assumptions are introduced in order to facilitate the estimation of energies at least to the correct signs. This paper examines in greater detail some of these additional assumptions using energy levels obtained by extended Hückel calculations as a basis for comparison. Since this comparison is facilitated by selecting systems having maximum symmetry and a minimum number of external orbitals to mix with the polyhedral core and surface bonding orbitals, the original Hoffmann-Lipscomb LCAO-MO extended Hückel calculations on the polyhedral borane anions $B_nH_n^{2-}$ are used¹³ selecting their results for the "3N problem" of the regular polyhedral $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$.

2. BACKGROUND

The topology of chemical bonding can be represented by a graph in which the vertices correspond to atoms or orbitals participating in the bonding and the edges correspond to bonding relationships. The adjacency matrix A of a graph, such as a graph representing chemical bonding, can be defined as follows:

$$A_{ij} = \begin{cases} 0 & \text{if } i=j \\ 1 & \text{if } i \text{ and } j \text{ are connected by an edge} \\ 0 & \text{if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (1)$$

The eigenvalues of the adjacency matrix are obtained from the following determinantal equation:

$$|A - xI| = 0 \quad (2)$$

where I is the unit matrix ($I_{ii} = 1$ and $I_{ij} = 0$ for $i \neq j$).

The eigenvalues of the adjacency matrix of the graph representing the relevant chemical bonding topology as determined by equation 2 are closely related to the energy levels as determined by Hückel theory.^{11,14,15,16} Thus Hückel theory uses the secular equation

$$|H - ES| = 0 \quad (3)$$

in which the energy matrix H and overlap matrix S can be resolved into the unit matrix I and the adjacency matrix A as follows:

$$H = \alpha I + \beta A \quad (4a)$$

$$S = I + \beta A \quad (4b)$$

The energy levels of the system are related to the eigenvalues of the adjacency matrix A (equation 2) as follows:

$$E = \frac{\alpha + x\beta}{1 + xS} \quad (5)$$

Thus a positive eigenvalue x of A corresponds to a bonding orbital and a negative eigenvalue x corresponds to an antibonding orbital in the corresponding chemical system. Furthermore, in Hückel theory S is taken to be zero and α is used as the zero of energy (i.e., set to zero). In this case

$$E = x\beta \quad (6)$$

and the energy levels are directly proportional to the eigenvalues of the adjacency matrix.

The polyhedral boranes discussed in this paper exhibit globally delocalized bonding.^{2,3} A vertex boron atom in such systems uses three of its four valence orbitals for intrapolyhedral bonding leaving one valence orbital as an external orbital to bond to the external group, typically a monovalent group such as hydrogen or halogen. One of the major triumphs of the graph-theory derived approach to the bonding topology in globally delocalized systems is the demonstration of the close analogy between the bonding in two-dimensional planar aromatic systems such as benzene and that in three-dimensional deltahedral boranes and carboranes.² In this context a deltahedron is defined as a polyhedron in which all faces are triangles. Thus consider a globally delocalized polygonal or deltahedral system having n vertices. In such a system the three internal orbitals on each vertex atom are divided into two twin internal orbitals (called "tangential" in some treatments¹⁷) and a unique internal orbital (called "radial" in some treatments¹⁷). Pairwise overlap between the $2n$ twin internal orbitals is responsible for the formation of the polygonal or deltahedral framework and leads to the splitting of these $2n$ orbitals into n bonding and n antibonding orbitals.

This bonding topology can be represented by a disconnected graph having $2n$ vertices corresponding to the $2n$ twin internal orbitals and n K_2 components where a K_2 component has two vertices with an edge connecting them. The dimensionality of this bonding of the twin internal orbitals is one less than the dimensionality of the globally delocalized system. Thus in the case of the two-dimensional planar polygonal systems such as benzene, the pairwise overlap of the $2n$ twin internal orbitals leads to the σ -bonding network which may be regarded as a collection of n one-dimensional bonds along the perimeter of the polygon involving adjacent pairs of polygonal vertices. The n bonding and n antibonding orbitals correspond to the σ bonding and σ^* antibonding orbitals, respectively. In the case of the three-dimensional deltahedral systems, the pairwise overlap of the $2n$ twin internal orbitals results in bonding over the two-dimensional surface of the deltahedron, which may be regarded as (topologically) homeomorphic to the sphere.

The equal numbers of bonding and antibonding orbitals formed by pairwise overlap of the twin internal orbitals are supplemented by additional bonding and antibonding molecular orbitals formed by global mutual overlap of the n unique internal orbitals. This bonding topology can be represented by a graph G in which the vertices correspond to the vertex atoms of the polygon or deltahedron or (equivalently) their unique internal orbitals and the edges represent pairs of overlapping unique internal orbitals. The relative energies of the additional molecular orbitals arising from such overlap of the unique internal orbitals are determined from the eigenvalues x of the adjacency matrix A of the graph G (see equations 2, 5, and 6, above). In the case of benzene the graph G is the C_6 graph (hexagon) which has three positive and three negative eigenvalues corresponding to the three π bonding and three π^* antibonding orbitals, respectively. In the case of a globally delocalized deltahedron having n vertices

such as found in the deltahedral boranes $B_nH_n^{2-}$ and the carboranes $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$), the graph G is the complete graph K_n in which each of the vertices has an edge going to every other vertex leading to a total of $n(n-1)/2$ edges. This corresponds to an n -center bond at the center (core) of the deltahedron formed by overlap of each unique internal orbital with every other unique internal orbital. The complete graph K_n has one positive eigenvalue, namely $n-1$, and $n-1$ negative eigenvalues, namely -1 each, regardless of the value of n indicating that the n -center core bond in a globally delocalized deltahedron leads to only one new bonding molecular orbital. The sum of the n bonding orbitals arising from the surface bonding of the twin internal orbitals and the single bonding orbital arising from the n -center core bonding of the unique internal orbitals gives a total of $n+1$ bonding orbitals for globally delocalized deltahedra having n vertices. Filling these $n+1$ bonding orbitals with electron pairs in the usual way gives a total of $2n+2$ bonding electrons in accord with the observed number of skeletal electrons required to form stable globally delocalized deltahedral boranes and carboranes.

The major objective of this paper is to examine how well the complete graph K_n approximates the core bonding in globally delocalized deltahedral systems. Thus, consider an octahedral borane such as $B_6H_6^{2-}$. The corresponding complete graph K_6 has $(6)(5)/2 = 15$ edges. Among these 15 edges, 12 represent overlap of the unique internal orbitals located on adjacent vertex atoms of the octahedron, namely a pair of atoms connected by one of the 12 edges. Such edges represent cis interactions. The remaining 3 edges of the K_6 graph represent overlap of the unique internal orbitals situated on one of the three pairs of antipodal vertices of the octahedron. Such edges represent trans interactions. Use of an unweighted K_6 graph to represent the core bonding topology in an octahedron gives equal weights to the cis and trans interactions despite their obvious geometric

difference. This problem was already recognized by Schmidtke in 1967 in one of the early papers pointing out the relationship between graph theory and Hückel theory.¹⁴ In group theoretical terms the graph theory derived model uses the symmetric group S_6 (i.e., the automorphism group of the complete graph K_6) rather than its subgroup O_h (i.e., the point group of the octahedron) to represent the symmetry of the skeletal bonding manifold of octahedral boranes such as $B_6H_6^{2-}$, which consists of the $6K_2$ surface bonding and the K_6 core bonding. The actual O_h rather than S_6 symmetry of these systems will result in partial or complete removal of the five-fold degeneracy of the core antibonding orbitals and the six-fold degeneracies of the surface bonding and antibonding orbitals.

A similar situation occurs in icosahedral boranes such as $B_{12}H_{12}^{2-}$. The corresponding complete graph K_{12} has $(12)(11)/2 = 66$ edges. Among these 66 edges, 30 edges represent overlap of the unique internal orbitals located on adjacent vertex atoms of the icosahedron, namely a pair of atoms connected by one of the 30 edges and corresponding to the ortho interaction using carborane nomenclature. An additional 30 edges of K_{12} represent overlap of the unique internal orbitals located on non-adjacent, non-antipodal vertex atoms of the icosahedron, namely the meta interaction. The remaining 6 edges of K_{12} represent overlap of the unique internal orbitals located on the 6 pairs of antipodal vertices of the icosahedron, namely the para interaction. Use of an unweighted K_{12} graph to represent the core bonding topology of an icosahedron gives equal weights to the ortho, meta, and para relationships despite their obvious geometric difference. The graph theory derived model thus uses the symmetric group S_{12} of order $12! = 479,001,600$ rather than the icosahedral group I_h of order 120 to represent the symmetry of the skeletal bonding manifold of icosahedral boranes such as $B_{12}H_{12}^{2-}$, which consists of the $12K_2$ surface bonding and the K_{12} core

bonding.

Reduction of the symmetry from that of the symmetric groups S_n ($n = 6$ or 12 , respectively) to the polyhedral groups O_h and I_h for octahedral and icosahedral boranes, respectively, not only splits some molecular orbitals of high degeneracies but also leads to some mixing of the core and surface bonding. Thus in the case of octahedral boranes under O_h symmetry the core bonding has the representation $A_{1g} + T_{1u} + E_g$ and the surface bonding has the representation $T_{1u} + T_{2g} + T_{2u} + T_{1g}$. The T_{1u} core and surface bonding molecular orbitals can therefore overlap leading to corresponding lowering and raising of the energies of the two molecular orbitals (designated as $\Delta E(T_{1u})$). Therefore, the T_{1u} orbital energies determined by computational methods based on O_h symmetry, including the extended Hückel method, do not correspond to pure core or surface bonding but also include the interaction $\Delta E(T_{1u})$, which represents another variable which needs to be evaluated before the graph theory derived methods can be compared with various computations. Thus in an octahedral borane such as $B_6H_6^{2-}$ under O_h symmetry, only the A_{1g} and E_g molecular orbitals can represent pure core bonding. In octahedral metal clusters in which external bonding orbitals clearly play a major role (e.g., $Co_6(CO)_14^{4-}$ studied by Mingos¹⁹), even the A_{1g} and E_g molecular orbitals do not represent pure core bonding because of interaction with other orbitals of A_{1g} and E_g symmetries arising from the external bonding.

A similar situation occurs for icosahedral boranes. Under I_h symmetry their core bonding has the representation $A_g + T_{1u} + T_{2u} + H_g$ and their surface bonding has the representation $T_{1u} + H_g + G_u + G_g + H_u + T_{1g}$. The T_{1u} and H_g core and surface bonding orbitals mix with energies $\Delta E(T_{1u})$ and $\Delta E(H_g)$, respectively, leaving only A_g and T_{2u} as pure core bonding orbitals.

This paper compares the graph-theory derived and Hückel theoretical models for $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ by determining which edge weights for the corresponding

K_n graphs retaining the polyhedral symmetries O_h and I_h , respectively, reproduce the energies for the pure core orbitals (A_{1g} and E_g for $B_6H_6^{2-}$ and A_g and T_{2u} for $B_{12}H_{12}^{2-}$) calculated by the extended Hückel method¹³ avoiding external orbitals (i.e., the "3N" set of Hoffmann and Lipscomb¹³) in order to eliminate core-external orbital mixing effects. These edge weights are then used to calculate hypothetical energies for the impure core orbitals (T_{1u} for $B_6H_6^{2-}$ and T_{1u} and H_g for $B_{12}H_{12}^{2-}$) in the absence of mixing (unperturbed core energies). Comparison of these hypothetical energies with the actual energies from the extended Hückel calculations¹³ allows evaluation of the core-surface mixing energies ($\Delta E(T_{1u})$ for $B_6H_6^{2-}$ and $\Delta E(T_{1u})$ and $\Delta E(H_g)$ for $B_{12}H_{12}^{2-}$). The assumptions of the simple graph theory derived bonding model can then be evaluated using the following observations:

- (1) The single positive eigenvalue of the complete K_n graphs should correspond to the completely symmetric (A_{1g} or A_g) core orbital being the only bonding orbital. All other core orbitals should have antibonding unperturbed core energies corresponding to the $n-1$ negative K_n eigenvalues.
- (2) The weights of the edges in the polyhedrally weighted K_n graphs representing non-adjacent vertices in the octahedron or icosahedron should be close to the unit weights taken for the edges in the K_n graphs representing adjacent vertices in the polyhedron.

The first observation is the important observation affecting applicability of the graph theory derived methods. Deviations of edge weights from unity are not serious if they do not create more than one positive eigenvalue for the core bonding.

3. THE OCTAHEDRON

Consider an octahedrally weighted K_6 complete graph having 12 edges of

unit weight corresponding to the octahedron edges and the remaining 3 edges of weight t corresponding to the three octahedron antipodal pairs. The spectrum of this graph can be determined by symmetry factoring²⁰ using a three-fold axis (Figure 1). The symmetric branch (A in Figure 1, top) gives the eigenvalue $4+t$ corresponding to the A_{1g} molecular orbital as well as one of the $-t$ eigenvalues of the triply degenerate T_{1u} molecular orbital. The doubly degenerate E branch gives the other two $-t$ eigenvalues of the triply degenerate T_{1u} molecular orbital as well as the two $-2+t$ eigenvalues of the doubly degenerate E_g molecular orbital. Note that any positive value of t is sufficient to lead to only one positive eigenvalue, namely the $4+t$ eigenvalue of the A_{1g} orbital, and five negative eigenvalues, namely the $-t$ eigenvalues of the triply degenerate T_{1u} orbitals and the $-2+t$ eigenvalues of the doubly degenerate E_g orbital. This indicates that any positive trans interaction in an octahedron gives the same distribution of bonding (1) and antibonding (5) orbitals as the unweighted K_6 graph used in the graph theory derived model² for $B_6H_6^{2-}$, $C_2B_4H_6$, and globally delocalized octahedral metal clusters. Thus for octahedral boranes and metal clusters the success of this model is not very dependent upon the value taken for t . Note also that setting $t = 0$ gives the spectrum of the octahedron (+4, 0, 0, 0, -2, -2) whereas setting $t = 1$ gives the spectrum of the K_6 complete graph (+5, -1, -1, -1, -1, -1).

The octahedron has two pure core bonding molecular orbitals, namely A_{1g} and E_g in the absence of mixing with external orbitals (see above). The computed values for the energies of these two orbitals substituted into equation 6 generate two equations in t and β ; these equations can be solved to determine these parameters provided that the zero energy level separating bonding and antibonding orbitals is known. Table 1 summarizes the results of such calculations using the energies computed by Hoffmann and Lipscomb¹³ for the "3N orbitals" of

$B_6H_6^{2-}$. Thus the computed energies for the A_{1g} and E_g core bonding molecular orbitals generate the following equations in t and β :

$$A_{1g}: (4+t)\beta = 2.969 \quad (7a)$$

$$E_g: (-2+t)\beta = -0.884 \quad (7b)$$

Solving these two equations gives $t = 0.625$ and $\beta = 0.642$. These values of t and β can then be used to calculate a hypothetical value for the T_{1u} core molecular orbital in the absence of core-surface interaction using the following equation:

$$T_{1u}: (-0.625)(0.642) = -0.401 \quad (8)$$

This compares with an energy of -0.829 found in the Hoffmann-Lipscomb calculation for the T_{1u} core orbital thereby indicating the interaction parameter $\Delta E(T_{1u})$ to be $-0.401 - (-0.829) = 0.428$. Applying this correction to the energy of the Hoffmann-Lipscomb calculation of the T_{1u} surface orbital gives energies of 0.595 and 0.493 for the bonding surface orbitals ($T_{1u} + T_{2g}$) and -0.416 and -0.671 for the antibonding surface orbitals ($T_{2u} + T_{1g}$). This distribution of the energies of the surface bonding orbitals is crudely consistent with the prediction by the graph theory derived method² of six bonding and six antibonding surface orbitals with the same absolute values for the energies arising from the spectra of six equivalent disconnected K_2 graphs.

Attempts have been made with much less success to apply this method to more recent computations on octahedral boranes and metal clusters. Armstrong, Perkins, and Stewart²¹ report self-consistent molecular orbital calculations on highly symmetrical borane cage anions including $B_6H_6^{2-}$. The zero energy

level of their calculation is not defined so that α as well as β and t are unknowns; thus equation 5 must be used rather than equation 6. This leads to an underdetermined system with only two equations to determine three unknowns; solution of this system to obtain meaningful numbers is not feasible.

The best example of a relevant calculation on a globally delocalized octahedral metal cluster is the Wolfsberg-Helmholtz molecular orbital calculation by Mingos¹⁹ on $\text{Co}_6(\text{CO})_{14}^{4-}$. However, because of the large number of external orbitals involved in this and other metal clusters, even the A_{1g} and E_g molecular orbitals do not represent pure core bonding. Thus the $\text{Co}_6(\text{CO})_{14}^{4-}$ system has three molecular orbitals of A_{1g} symmetry and four molecular orbitals of E_g symmetry thereby precluding an analysis of the type given above for the Hoffmann-Lipscomb $\text{B}_6\text{H}_6^{2-}$ computation.

4. THE ICOSAHEDRON

Consider an icosahedrally weighted K_{12} complete graph having 30 edges of unit weight corresponding to the icosahedron edges, 30 edges of weight m corresponding to the meta interaction of non-adjacent non-antipodal vertex pairs, and 6 edges of weight p corresponding to the para interaction of the 6 icosahedron antipodal pairs. The spectrum of this graph can be determined by symmetry factoring using first a three-fold axis and then a two-fold axis (Figure 1, bottom). The fully symmetric branch (A_g) gives the eigenvalue $5+5m+p$ corresponding to the A_g molecular orbital as well as one of the $-1-m+p$ eigenvalues of the quintuply degenerate H_g molecular orbitals. The remaining four $-1-m+p$ eigenvalues of the quintuply degenerate H_g molecular orbitals arise from the two isolated vertices of the doubly degenerate E_g branch. The A_u branch and the doubly degenerate E_u branch generate a quadratic equation whose roots

give the eigenvalues of the triply degenerate T_{1u} and T_{2u} molecular orbitals. Note that the T_{1u} molecular orbital has a positive eigenvalue unless $p > \sqrt{5}(1-m)$. Thus with most likely values of the edge weights m and p the icosahedrally weighted K_{12} graph (Figure 1) has four positive eigenvalues (the A_g and triply degenerate T_{1u} orbitals) rather than only the single positive eigenvalue characteristic of the unweighted K_{12} graph. Note also that setting $m=0$ and $p=0$ gives the spectrum of the icosahedron $(+5, +\sqrt{5}, +\sqrt{5}, +\sqrt{5}, -1, -1, -1, -1, -1, -1, -\sqrt{5}, -\sqrt{5})$ whereas setting $m=1$ and $p=1$ gives the spectrum of the K_{12} complete graph $(+11, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1)$.

The icosahedron like the octahedron has two pure core bonding molecular orbitals, namely A_g and T_{2u} . The computed values for their energies substituted in equation 6 generate two equations in the three parameters m , p , and β . The system is therefore underdetermined and an additional relationship between m , p , and β must be used in order to obtain unique values for the three parameters. Instead of assuming such a relationship, consider the minimum value of p to be zero and the maximum value of p to be m . Then plot against p in this range the corresponding values of the parameters m and β (Figure 2) and the molecular orbital energy levels adjusted by removal of the core-surface interaction (Figure 3) using the data from the Hoffmann-Lipscomb 3N extended Hückel computations on $B_{12}H_{12}^{2-}$. The values of β and the core molecular orbital energies are seen from Figures 2 and 3 to be rather insensitive to the actual value of p taken.

By far the most important conclusion from these data is that for all likely values of p the core bonding in icosahedral $B_{12}H_{12}^{2-}$ leads to four positive eigenvalues ($A_{1g} + T_{1u}$) rather than the single positive eigenvalue obtained by using the K_{12} complete graph for the core bonding topology. The graph theory derived model² is thus incorrect for the icosahedron since it leads to the wrong number of positive eigenvalues for the core bonding, namely one rather than

four. Nevertheless, the graph theory derived model works for icosahedral boranes and carboranes because this fundamental error is corrected by mixing the bonding T_{1u} core orbitals with the bonding T_{1u} surface orbitals. Thus the mixing energy $\Delta E(T_{1u})$ is so large (1.1 to 1.6 on the scale of Table 2) that the core T_{1u} orbitals are raised to antibonding energies by the core-surface interaction so that only one core bonding orbital, namely the A_g orbital, remains after this interaction. This is why the graph theory derived model for icosahedral $B_{12}H_{12}^{2-}$ leads to the experimentally observed skeletal electron count even though the assumption of the K_{12} complete graph for the core bonding topology leads to the incorrect number of core bonding orbitals (before core-surface mixing).

Important experimental support for these ideas is found in the centered icosahedral gold cluster $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$ (ref. 22) in which there is no surface bonding comparable to that of $B_{12}H_{12}^{2-}$ because the p orbitals of the 12 peripheral gold atoms in this cluster have energies too high to function as twin internal orbitals for surface bonding.^{6,7} Turning off the surface bonding in this way in the centered icosahedral $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$ leads to four core bonding orbitals in accord with the energy levels of the icosahedrally distorted K_{12} graph for any reasonable levels of the parameters m and p (Figure 1 bottom and Figure 3). This point may also relate to the general observation⁶ that the overlap topology of the n-1 peripheral gold atoms in a centered Au_n cluster leads to electron counts corresponding not to those expected for a K_{n-1} complete graph but instead to that of the polyhedron formed by the peripheral gold atoms.

5. SUMMARY

Determination of the eigenvalues of the octahedrally weighted K_6 complete graph indicates one positive eigenvalue for any positive weighting (t) of the

antipodal (trans) interactions relative to unit adjacent (cis) interactions. This indicates that the unweighted K_6 graph used in the graph theory derived model for the octahedral boranes, carboranes, and metal clusters² is adequate for determining the correct number of core bonding orbitals and therefore the corresponding electron counts. The Hoffmann-Lipscomb calculations¹³ on $B_6H_6^{2-}$ correspond to a value of 0.625 for this parameter t .

A similar determination of the eigenvalues of the icosahedrally weighted K_{12} complete graph indicates four positive eigenvalues for any likely values for the weighting parameters m and p . This is in disagreement with the graph theory derived model² for icosahedral boranes and carboranes which uses the unweighted K_{12} graph for the core bonding leading to only a single positive eigenvalue corresponding to a single core bonding orbital. However, core-surface bonding interactions raise the energies of three of the four core bonding orbitals to antibonding levels so that despite this major inaccuracy the graph theory derived model fortuitiously gives correct electron counts for icosahedral boranes.

The analysis in this paper shows that the graph theory derived model² describes a bonding topology which is accurate enough to lead to correct electron counts in octahedral clusters but leads to difficulties in icosahedral clusters. However, most globally delocalized metal clusters fortunately are octahedra to which this simple bonding approach can be reliably applied. It thus appears that the graph theory derived models will continue to be useful in understanding the relationship between shape and electron count in the large variety of known polyhedral boranes, carboranes, and metal clusters.

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TABLE 1
MOLECULAR ORBITAL ENERGY PARAMETERS
FOR OCTAHEDRAL $B_6H_6^{2-}$

<u>Molecular Orbital</u>	<u>Calculated by Hoffmann and Lipscomb^a(3N)</u>	<u>Adjusted by Removal of Core- Surface Interaction</u>
<u>Core Bonding</u>		
A_{1g}	2.969	2.969
T_{1u}	-0.829	-0.401
E_g	-0.884	-0.884
<u>Surface Bonding</u>		
T_{1u}	1.023	0.595
T_{2g}	0.493	0.493
T_{2u}	-0.416	-0.416
T_{1g}	-0.671	-0.671
<u>Other Parameters</u>		
β	0.642	0.642
t	0.625	0.625
$\Delta E(T_{1u})$	0.428	0

a) From R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36, 2179 (1962).

TABLE 2

MOLECULAR ORBITAL ENERGY PARAMETERS FOR ICOSAHEDRAL $B_{12}H_{12}^{2-}$

Molecular Orbital	Calculated by Hoffmann and Lipscomb ^a (3N)	Adjusted by Removal of Core-Surface Interaction $m=0.355, p=0$	$m=0.4, p=0.2$	$m=p=0.466$
<u>Core Bonding</u>				
Ag	4.163	4.163	4.163	4.163
T _{1u}	-0.773	0.855	0.658	0.388
Hg	-0.856	-0.832	-0.692	-0.534
T _{2u}	-0.886	-0.886	-0.886	-0.886
<u>Surface Bonding</u>				
T _{1u}	1.907	0.249	0.476	0.746
Hg	0.984	0.960	0.820	0.662
G _u	0.518	0.518	0.518	0.518
G _g	-0.471	-0.471	-0.471	-0.471
H _u	-0.678	-0.678	-0.678	-0.678
T _{1g}	-0.782	-0.782	-0.782	-0.782
<u>Other Parameters</u>				
β		0.614	0.575	0.534
$\Delta E(T_{1u})$		1.658	1.431	1.161
$\Delta E(Hg)$		0.024	0.164	0.322

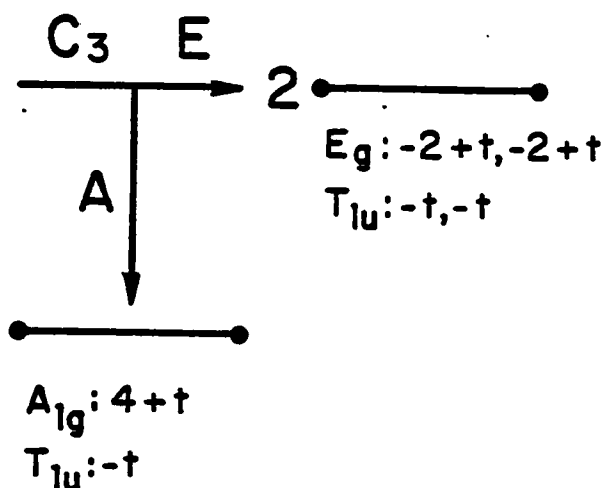
Figure 1: Symmetry factoring schemes for the octahedrally weighted K_6 graph (top) and the isocahedrally weighted K_{12} graph (bottom). The designations of the branches correspond to that used in R.B. King, Theor. Chim. Acta, **44**, 223 (1977). The symmetry factoring of the octahedrally weighted K_6 graph uses a three-fold axis (C_3) leading to an A branch and a doubly degenerate E branch. The symmetry factoring of the icosahedrally weighted K_{12} graph first uses a three-fold axis (C_3) similarly leading to A and doubly degenerate E branches, which in turn use two-fold axes (C_2) for further symmetry factoring into symmetric (G) and antisymmetric (U) branches; the resulting four branches are designated as AG, AU, EG, and EU.

Figure 2: Plot of the parameters m and β versus p for the Hoffmann-Lipscomb 3N extended Hückel computations on $B_{12}H_{12}^{2-}$.

Figure 3: Plot of the energies of the core molecular orbitals $A_g + T_{1u} + T_{2u} + H_g$ versus p in the absence of core-surface interactions for the T_{1u} and H_g orbitals for the Hoffmann-Lipscomb 3N extended Hückel computations on $B_{12}H_{12}^{2-}$.

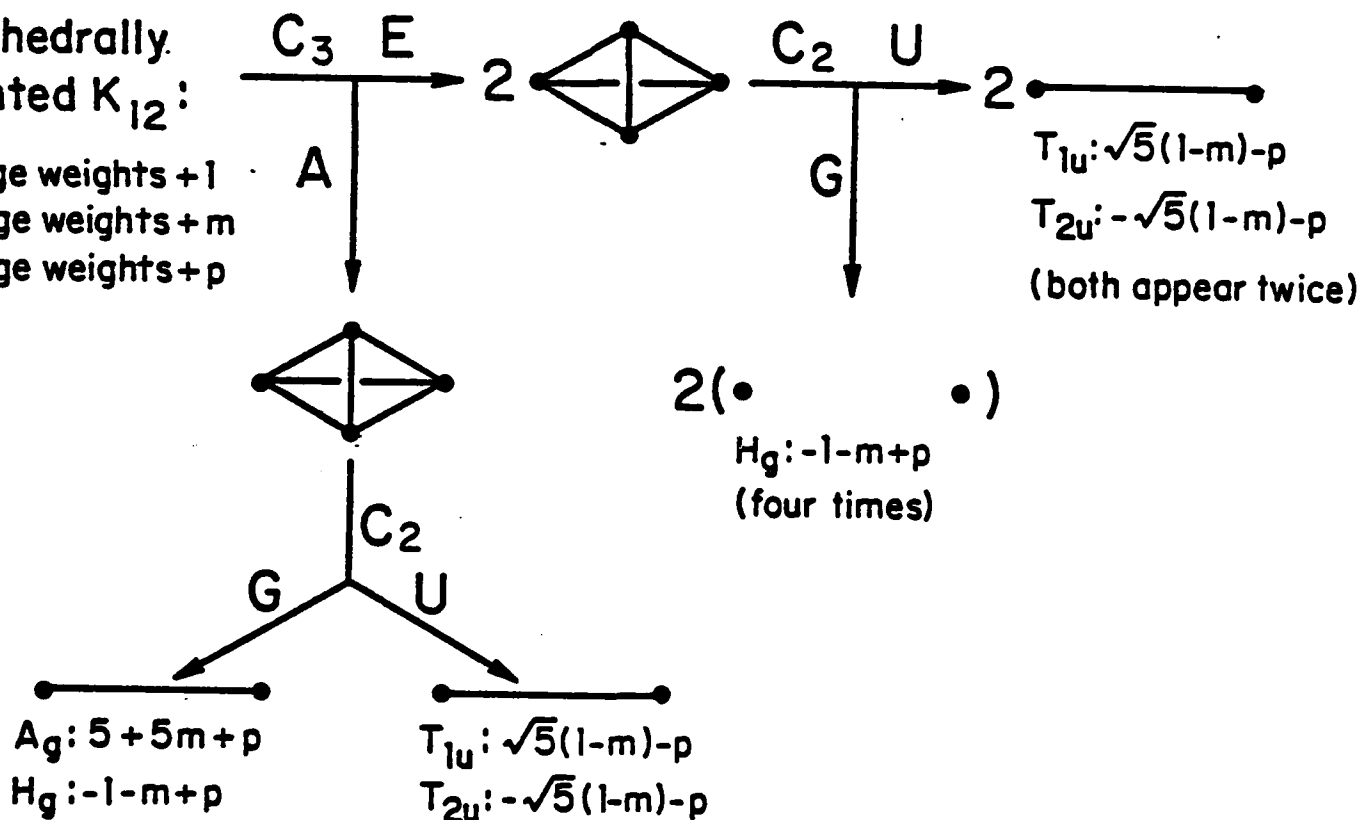
Octahedrally
weighted K_6 :

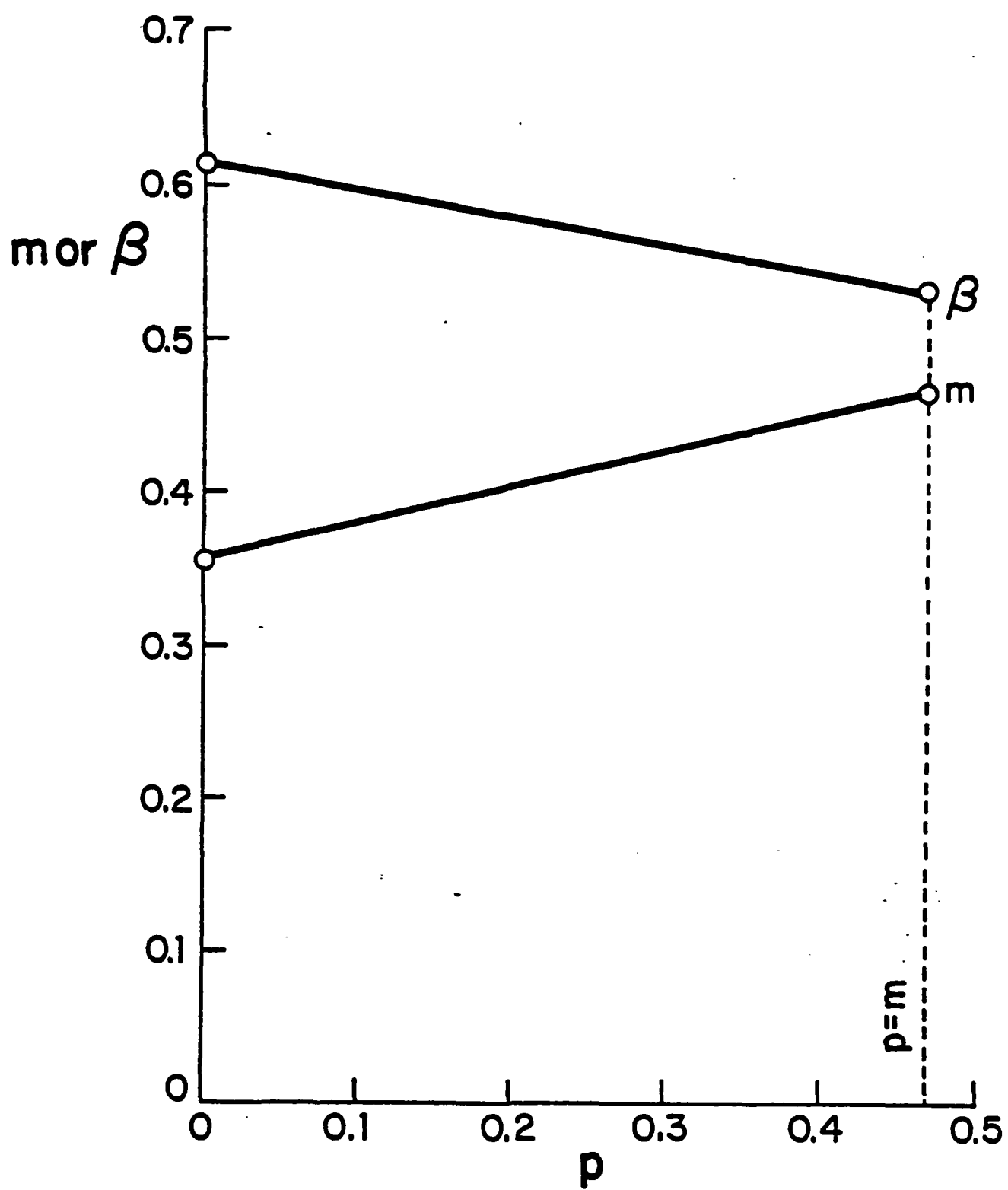
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3 edge weights +t

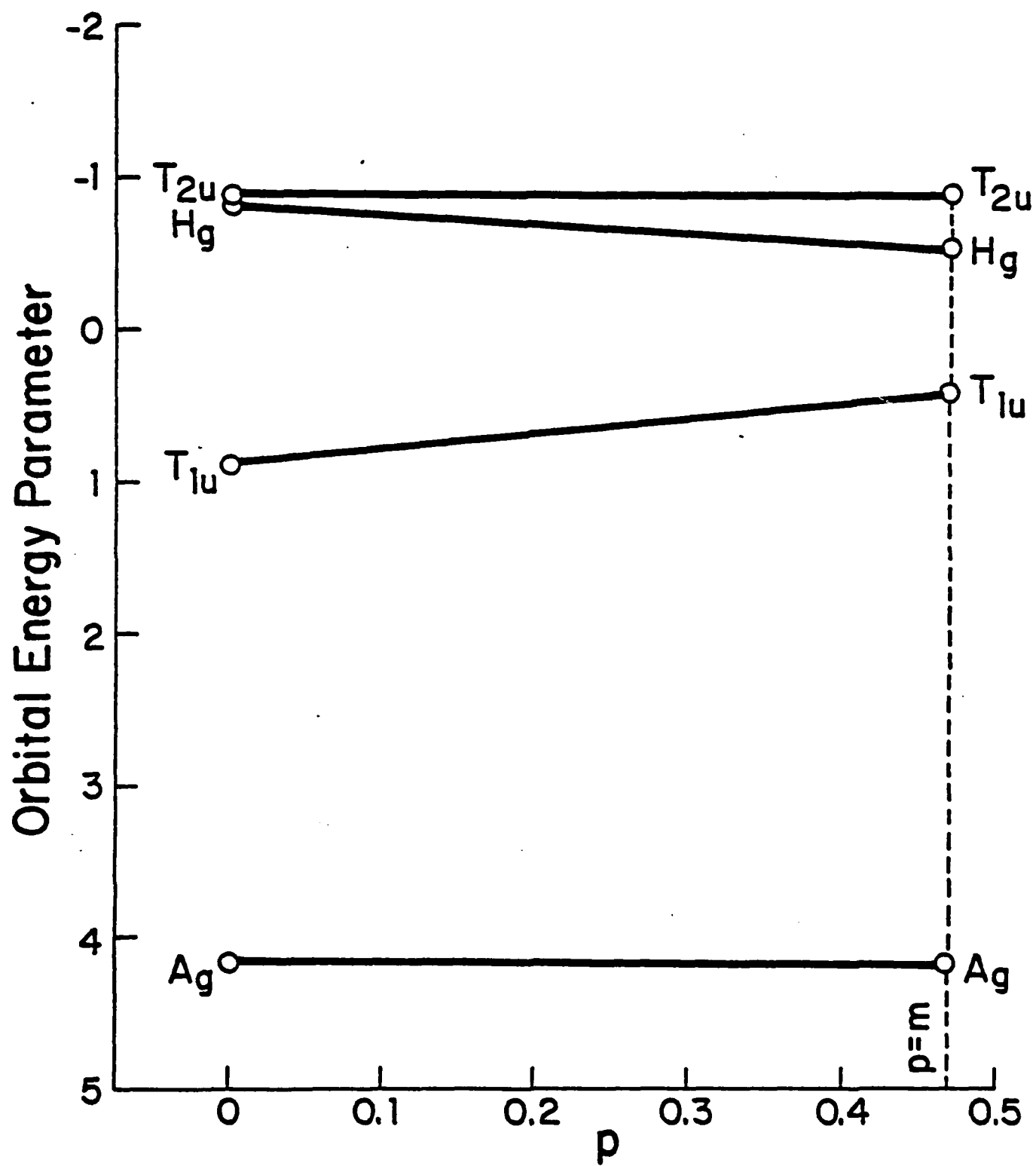


Icosahedrally
weighted K_{12} :

30 edge weights +1
30 edge weights +m
6 edge weights +p

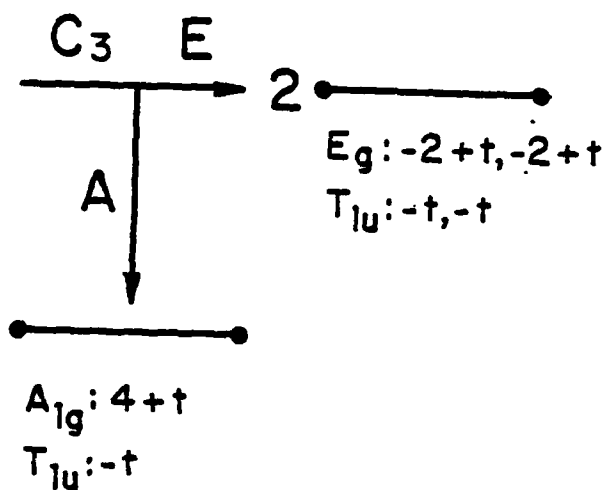






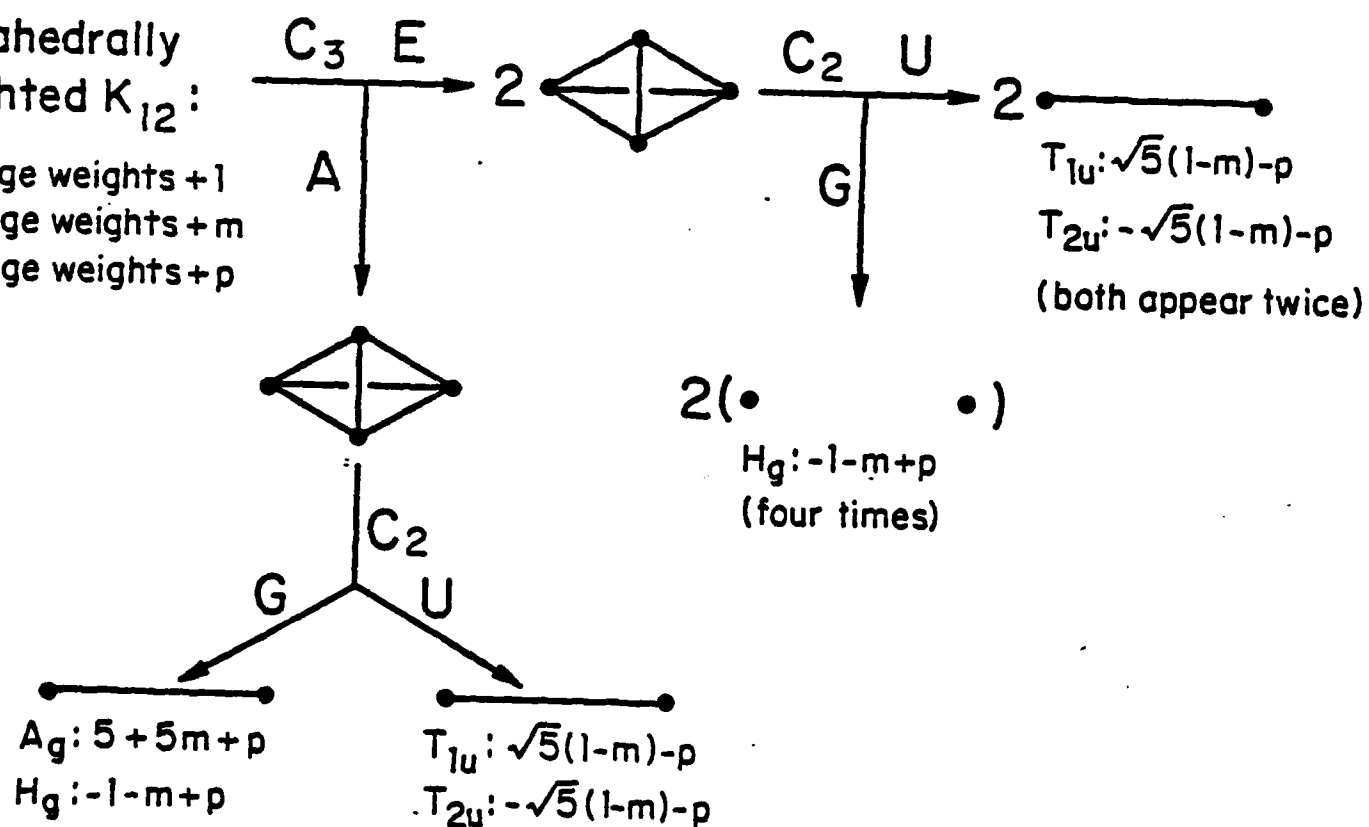
Octahedrally
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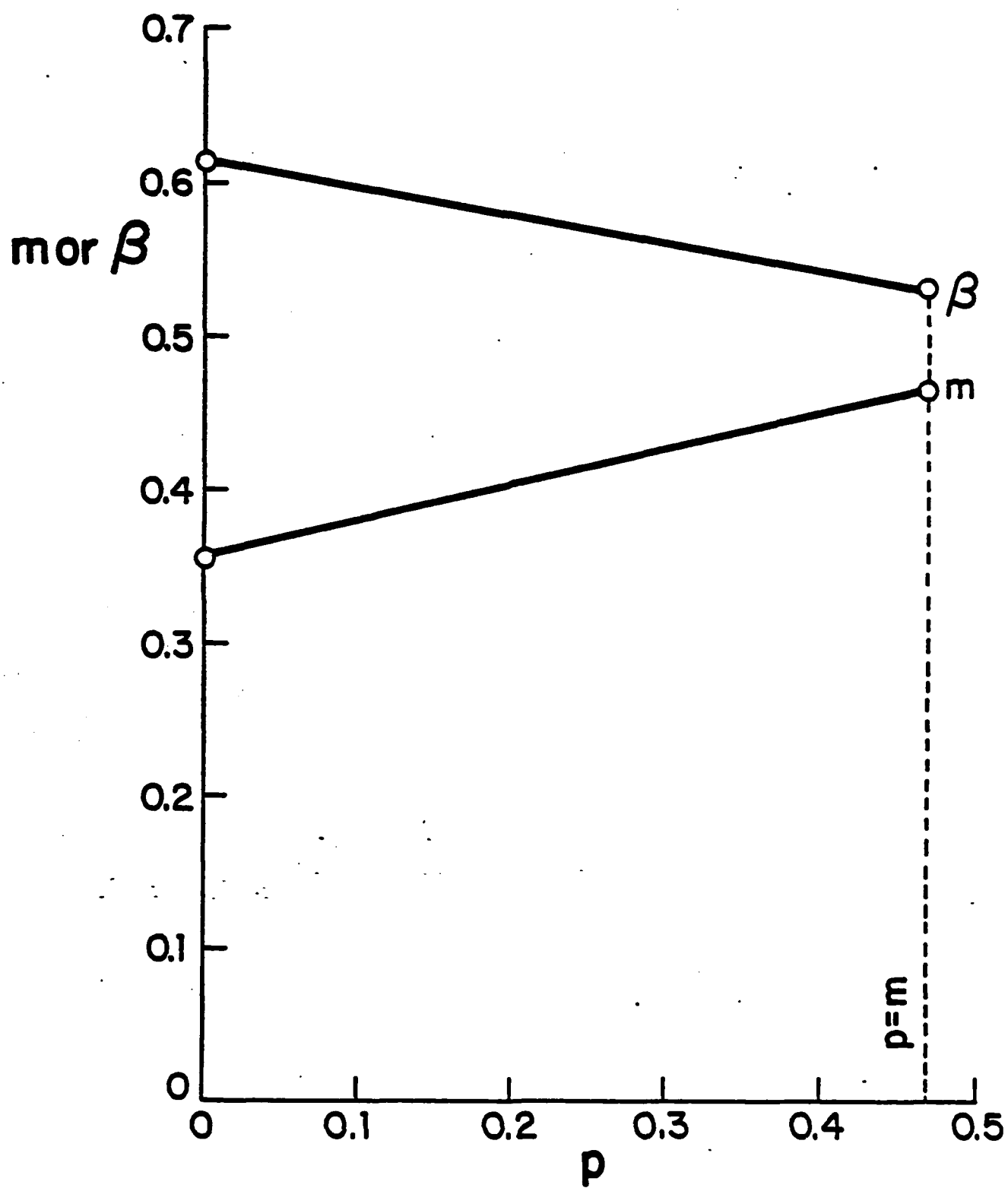
12 edge weights +1
3 edge weights +t

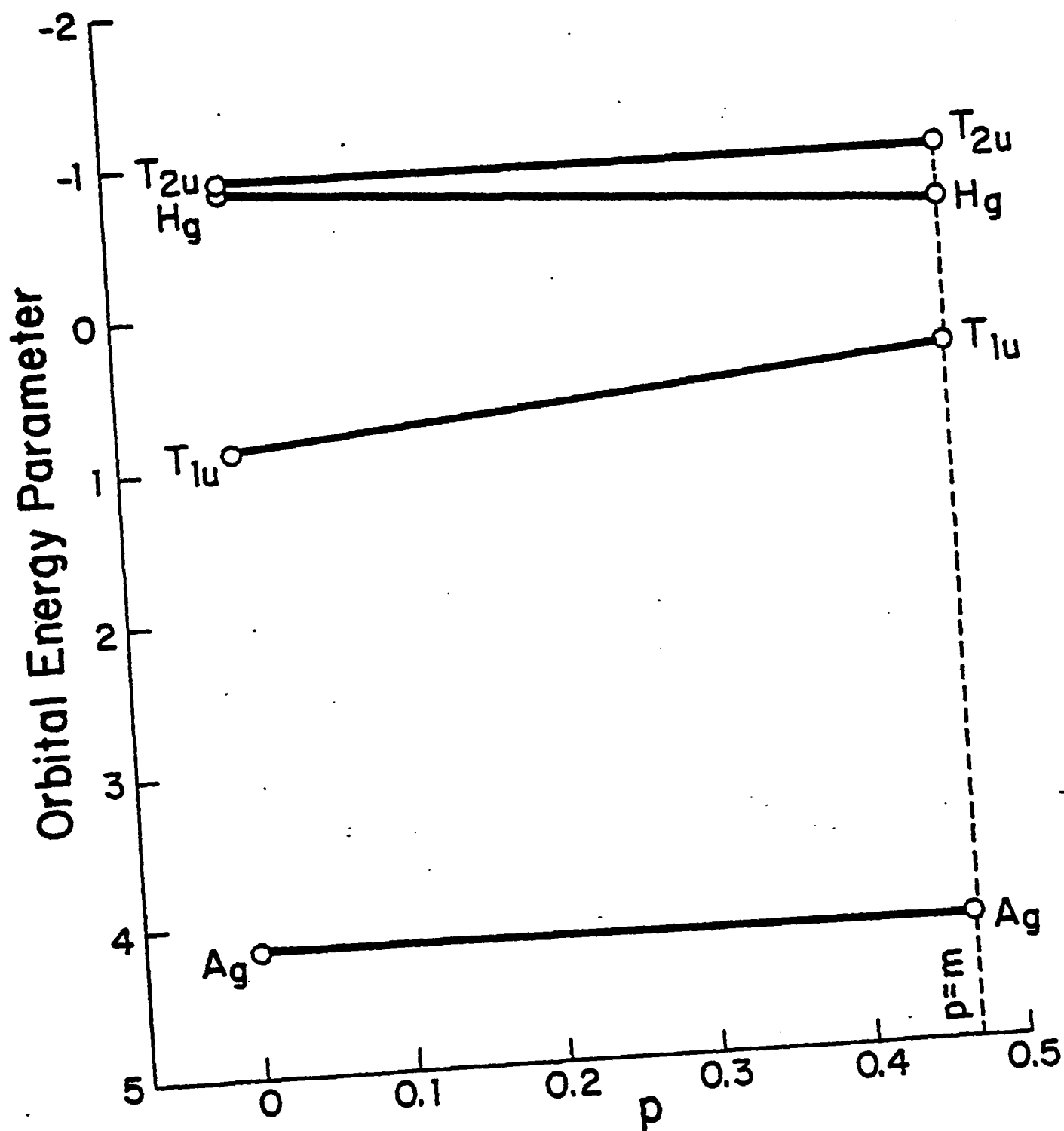


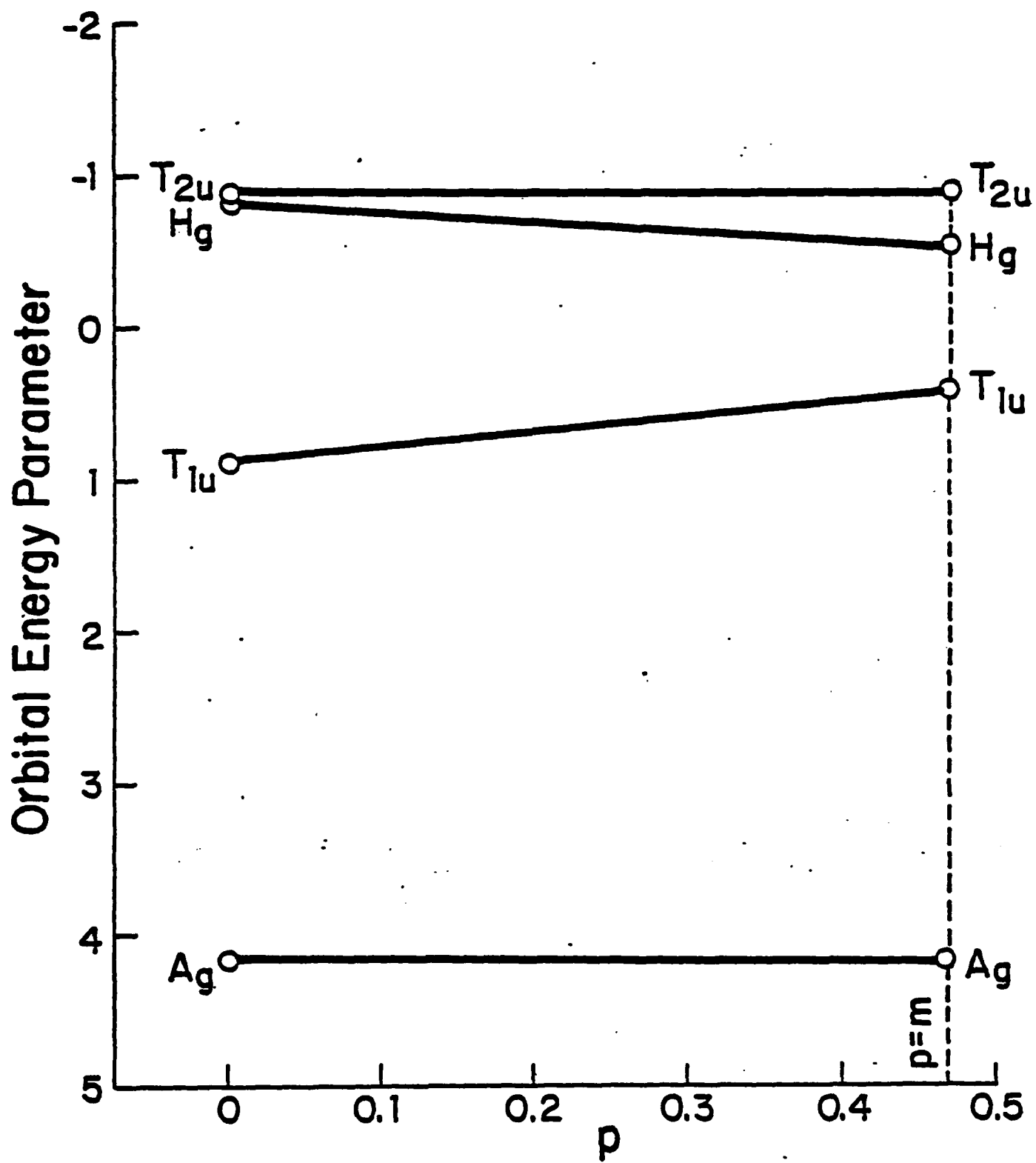
Icosahedrally
weighted K_{12} :

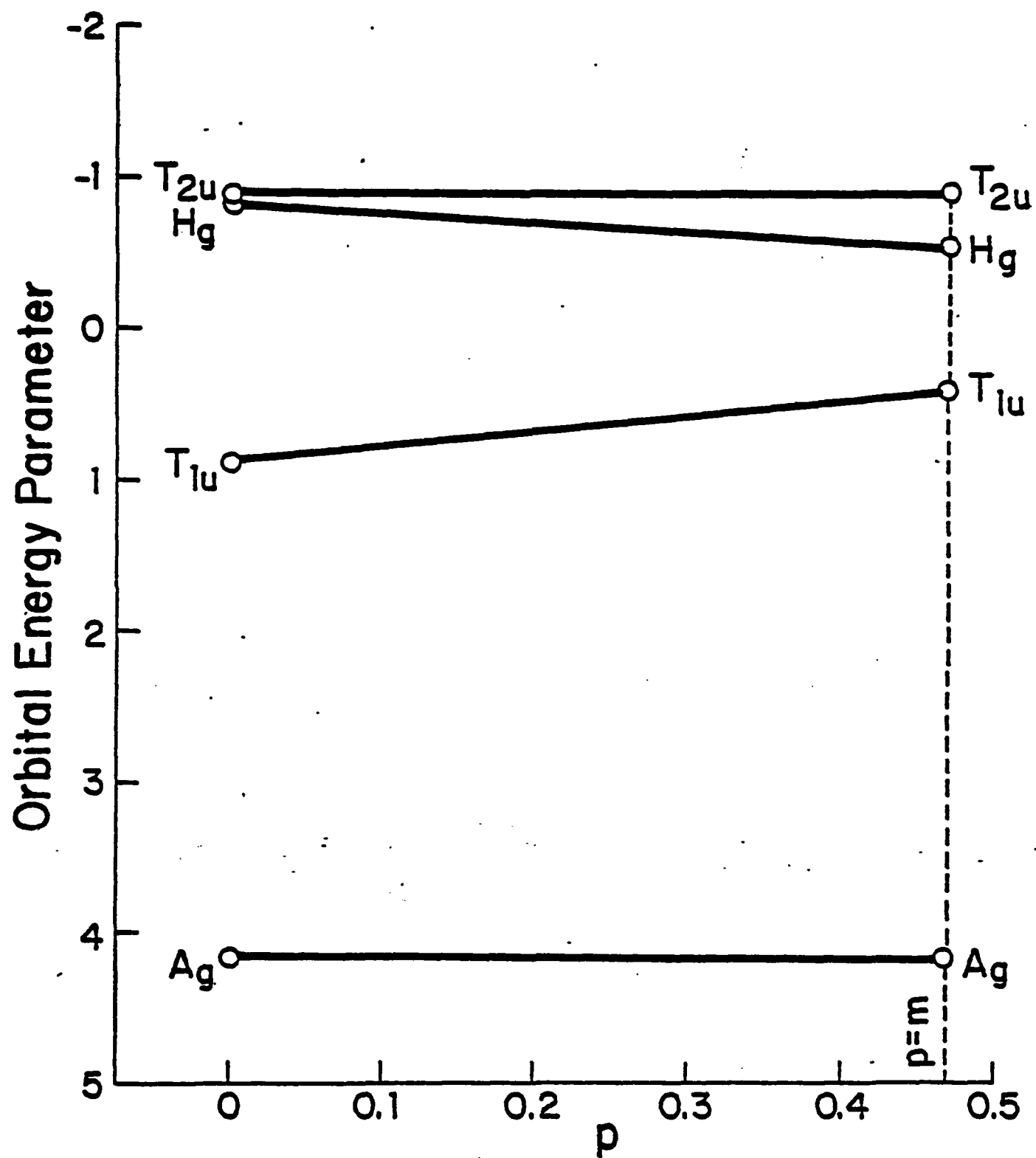
30 edge weights +1
30 edge weights +m
6 edge weights +p











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